

sibly is tridymite. In bulk it forms about a third part of the mixed crystalline mass.

The crystals are very imperfect, and are twinned: but there are two cleavages parallel to the planes of a prism of about 119° ; and, on looking through a plane that is perpendicular to this zone, it is seen that the crystal is biaxial. The normal to this plane is parallel to the second mean line, the optical character being negative.

A section made for examination in the microscope showed two small crystals in which light traverses the section with equal brilliancy during its rotation between crossed Nicol prisms. This, and possibly a similar case recorded by Vom Rath, seems to result from the section being cut parallel to a composite portion of the crystal.

The analysis of the mineral gave, by distillation of the silica as silicic difluoride, and subsequent determination as potassic fluosilicate, 97.43 per cent. of silica, the remainder being oxide of iron and lime. Thus 0.3114 grm. gave:

| | | per cent. |
|------------------------|---------------|---------------|
| Silica | 0.3034 | 97.43 |
| Ferric oxide | 0.0035 | 1.124 |
| Lime | 0.0018 | 0.578 |
| | <u>0.3087</u> | <u>99.132</u> |

A second analysis gave 99.21 per cent. silica, 0.79 of residue.

Its specific gravity, as determined from a very small amount of the mineral picked under the microscope, was 2.18; a second determination made on a larger amount gave the value 2.245. That of tridymite is 2.295 to 2.3. This may be taken as evidence that the mineral is not quartz, the specific gravity of which is 2.65. Vom Rath's experiments were made on a rather less pure form of tridymite.

There can be no doubt from these results, further details of which shall be shortly laid before the Society, that this mineral is silica in the form of its allotropic condition and lower density. It may possibly be the mineral to which Vom Rath has given the name of Tridymite; the crystalline system, however, of Tridymite, as given by Vom Rath, does not accord with the above facts.

II. "On the Derivatives of Propane (Hydride of Propyl)." By C. SCHORLEMMER. Communicated by Prof. STOKES, Sec. R.S Received March 5, 1869.

At the time when I commenced this investigation, the existence of normal propyl alcohol was very doubtful. According to Chancel*, this body is found in the fusel-oil from the marc of grapes; but Mendeleeff† tried in vain to isolate it from a sample of this oil which he had obtained

* Compt Rend. vol. xxxvii. p. 410.

† Zeitschrift für Chemie, 1868, p. 25.

from Chancel himself. Several attempts to prepare the normal alcohol by synthesis failed. Thus Linnemann and Siersch* tried to obtain it by converting acetonitril into propylamine, by means of hydrogen in the nascent state, and decomposing the hydrochlorate of this base with silver nitrite; but the alcohol thus formed was found to be the secondary one. The same compound was obtained by Butlerow and Ossokin†, by acting upon ethylene iodohydrine, $C_2H_4 \begin{Bmatrix} OH \\ I \end{Bmatrix}$, with zinc methyl, in order to replace iodine by methyl. Now as in both cases, according to theory, the normal or primary alcohol ought to have been formed, and as we have no explanation why instead of this compound the secondary alcohol was obtained, Butlerow and Ossokin believe that the normal propyl-alcohol cannot exist. Not agreeing with this view, I was led to an investigation of this subject, the results of which I have the honour to lay before the Society.

My reasoning was as follows:—It appears, as the most probable theory, and which is now accepted by most chemists, that the four combining powers of the carbon atom have the same value. If so, only one hydrocarbon having the composition C_3H_8 can exist. This *propane* must be formed by replacing the iodine in the secondary propyl iodide, by hydrogen, and subjecting the hydrocarbon thus obtained to the action of chlorine, by which primary propyl chloride must be formed in accordance with the behaviour of other hydrocarbons of the same series.

I soon found that my theory was correct; and in a short note, which I published in 'Zeitschrift für Chemie' (1868, p. 49), I stated that I had obtained the normal propyl alcohol by this method. At the same time, Fittig proved that it was contained in fusel-oils‡, and lately Linnemann prepared it synthetically from ethyl-compounds by converting acetonitrile (ethyl cyanide) into propionic anhydride, and acting upon this body with nascent hydrogen§.

The propane which I used in my researches was obtained by acting upon isopropyl iodide with zinc turnings and diluted hydrochloric acid. A continuous evolution of gas takes place if the flask containing the mixture is kept cold. If it is not cooled down a violent reaction soon sets in. The gas always contains vapour of the iodide, even if it has been evolved very slowly. In order to purify it as much as possible, it was washed with Nordhausen sulphuric acid, with a mixture of nitric and sulphuric acids and with caustic soda solution.

As a gas-holder I used a tubulated bell-jar, which was suspended in a larger inverted one, filled with a concentrated solution of common salt. When a sufficient quantity of gas had collected, chlorine was passed into

* Annalen Chem. Pharm. vol. cxliv. p. 137.

† *Ibid.* vol. cxlv. p. 257.

‡ Zeitschrift für Chemie, 1868, p. 44.

§ Annalen Chem. Pharm. vol. cxlviii. p. 251.

it, care being taken not to have it in excess. In diffused daylight substitution-products were formed, which collected as an oily layer on the salt solution. Alternately more propane and chlorine were passed into the apparatus, until it was nearly filled with the excess of propane and vapours of the most volatile substitution-products. The latter were condensed by passing the gas into a receiver surrounded by a freezing-mixture. To collect the liquid chlorides which were contained in the gas-holder, the tubulus of the bell-jar was closed with cork, which was provided with a wide short glass tube, open at both ends, and so much salt solution put into the gas-holder that the chlorides entered this tube, from which they could easily be removed with a pipette. By repeating this process several times, a quantity of chlorine compounds, sufficient for further investigation, was obtained. This was washed with water, dried over caustic potash, and distilled. The liquid commenced to boil at $42^{\circ}\text{C}.$, the boiling-point rising towards the end above $200^{\circ}\text{C}.$ By fractional distillation, a comparatively small quantity of a liquid was obtained, which boiled at 42° – 46° , and consisted of the primary propyl chloride, $\text{C}_3\text{H}_7\text{Cl}$.

0.0975 of this chloride gave 0.1730 silver chloride, and 0.005 silver, corresponding to 0.044 chlorine.

Calculated for $\text{C}_3\text{H}_7\text{Cl}$.

45.2 per cent. Cl.

Found.

45.5 per cent. Cl.

In order to prove that this body was really the normal chloride, it had to be converted into the alcohol. For this purpose I used that portion of the chlorides which, after repeated distillation, boiled below $80^{\circ}\text{C}.$ It was heated in sealed tubes with potassium acetate and glacial acetic acid for several hours to $200^{\circ}\text{C}.$, and thus converted into the acetate, a light colourless liquid, possessing the characteristic odour of the acetic ethers. I did not endeavour to obtain this ether in the pure state, as this could have been effected only with great loss of material, but converted it at once into the alcohol, by heating it with a diluted solution of potash, in sealed tubes, up to $120^{\circ}\text{C}.$ After cooling, the contents of the tubes were distilled and rectified. A portion of it was oxidized with a cold diluted solution of chromic acid. No gas was evolved, but a strong smell of aldehyde was perceived, which disappeared on adding more chromic acid. On distilling to dryness, an acid liquid was obtained, which was neutralized with sodium carbonate. The solution was evaporated to dryness, and the residue distilled with a quantity of sulphuric acid, sufficient to liberate about one-fourth of the acid. The residue in the retort was again distilled with the same quantity of sulphuric acid, and, by repeating this process, the acid was obtained in four fractions. Each of these was converted into the silver-salt by boiling with silver carbonate. The silver-salts crystallized from the hot saturated solution in small shining needles, which were grouped in stars and feathers. These were dried, first, over sulphuric acid, afterwards in the steam-bath, and the silver determined by ignition.

| | | | | per cent. |
|----------------------------|--------|------|--------|--------------|
| Fraction (1) | 0·2350 | gave | 0·1404 | silver=59·74 |
| „ (2) | 0·2420 | „ | 0·1450 | „ =59·91 |
| „ (3) | 0·1676 | „ | 0·1002 | „ =59·78 |
| „ (4) | 0·2124 | „ | 0·1264 | „ =59·51 |
| Mean | | | | 59·73 |
| Silver propionate contains | | | | 59·67 |

I also prepared the lead-salt, which exhibited the properties of lead-propionate; it did not crystallize, but dried up to an amorphous gum-like mass. As by oxidation no other acid besides propionic was found, it follows that the alcoholic liquid could only contain normal propyl alcohol. I tried to isolate this body from the remaining liquid, by adding potassium carbonate until it separated into two layers. The upper one was taken off and dried, first over fused potassium carbonate, and afterwards over anhydrous baryta. This liquid, however, proved to be a mixture; it began to boil at 80° C., and the boiling-point rose slowly to 96° C. By fractionating it could be separated into two portions—a smaller one boiling between 80°–85°, and a larger one boiling above 90°. The portion boiling between 92°–96° gave, by combustion, numbers agreeing with the composition of propyl alcohol.

0·2238 substance gave 0·4098 carbon dioxide and 0·2675 water.

| | Calculated. | | Found. |
|----------------|-------------|--------|--------|
| C ₃ | 36 | 60 | 59·81 |
| H ₈ | 8 | 13·33 | 13·28 |
| O | 16 | 26·67 | — |
| | 60 | 100·00 | |

I have not yet studied the properties of this alcohol, as I hope to obtain it soon in larger quantities.

The liquid boiling between 80°–85° appears to be an acetal; it is not acted upon by sodium, and therefore can easily be obtained free from alcohol, by distilling it over this metal. The small quantity was just sufficient for two analyses, the results of which give C₅ H₁₂ O₂ as the probable formula.

(1) 0·2500 gave 0·2725 water and 0·5280 carbon dioxide.

(2) 0·2755 gave 0·2950 water; the determination of carbon was lost.

| | Calculated. | | Found. | |
|-----------------|-------------|--------|--------|-------|
| | | | I. | II. |
| C ₅ | 60 | 57·96 | 57·60 | — |
| H ₁₂ | 12 | 11·53 | 12·11 | 11·93 |
| O ₂ | 32 | 30·78 | — | — |
| | 104 | 100·00 | | |

How this body has been formed I cannot explain.

As I have already mentioned, chloride of propyl forms only a small fraction of the products obtained by subjecting propane to the action of

chlorine, the chief product of the reaction being a liquid which boils at 94° – 98° C., and has the formula $C_3H_6Cl_2$.

0.1600 gave 0.3970 silver chloride and 0.005 silver.

Calculated for $C_3H_6Cl_2$.

62.8 per cent. Cl.

Found.

62.4 per cent.

This body is propylene dichloride; for its boiling-point not only coincides with that of this compound, but also all its reactions are the same. Heated with potassium acetate and acetic acid in closed tubes, it is readily decomposed, a high boiling acetate being formed, which, on heating with concentrated potash solution and distilling, yields a liquid the last portion of which boils between 180° – 190° C., and possesses the sweet taste of propyl glycol. I did not isolate the glycol in the pure state, but proposed to establish its structure by oxidation.

A diluted cold solution of chromic acid acts violently on it, carbon dioxide being evolved in abundance, and a strong odour of aldehyde being recognized, which, on further addition of the oxidizing liquid, was changed into that of acetic acid. By distillation an acid liquid was obtained, which, on boiling with silver carbonate, yielded a silver-salt, which crystallized in the well-known needles of silver acetate.

0.3013 of this salt left on ignition 0.1935 silver.

Silver acetate contains

64.67 per cent Aq.

Found.

64.22 per cent.

The oxidation-products (carbon dioxide and acetic acid) prove sufficiently that the structure of the glycol is expressed by the formula $CH_3-CH(OH)-CH_2(OH)$, which is that of the known propyl glycol.

The foregoing researches establish a general reaction for converting secondary compounds of the alcohols into those of primary radicals. This is effected by replacing the iodine in secondary iodides by hydrogen, and subjecting the hydrocarbons thus obtained to the action of chlorine, by which the primary chlorides are formed.

Of greater interest, perhaps, as possessing an important bearing on the theory of substitution, is the fact that the second substitution-product of propane consists of propylene dichloride, having the structure $CH_3-CHCl-CH_2Cl$. This was the less to be expected, as ethane, C_2H_6 , the hydrocarbon next lower in the series, yields, by acting on it with chlorine as second product, ethylidene dichloride, CH_3-CHCl_2 . Whilst, therefore, in propane first one hydrogen atom in the methyl group is replaced by chlorine, and afterwards one which is combined with the adjoining carbon atom, in ethane the substitution takes place at one and the same carbon atom. The action of chlorine upon propane is certainly in contradiction to all theories of substitution which have been expounded.

In a second communication I propose to describe the higher chlorinated substitution-products of propane.